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MECHANICAL RECYCLING OF SHORT CARBON FIBERS AND GROUND CARBON FIBERS REINFORCED PA66

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Summary: Fiber-reinforced polymer composites occupy a fair share of structural and lightweight applications, replacing traditional materials whenever possible. Along with many advantages they offer, such as excellent mechanical properties to weight ratio, low price, fast production, the possibility of tailoring the properties for specific applications, etc. On the other hand, at the end of their lifetime, they are usually disposed of in landfills. Carbon fiber polymer composites (CFRPs) are relatively expensive materials and should be considered for recycling and reuse. Therefore, the influence of multiple cycles of mechanical recycling through grinding and injection molding was studied. PA66, PA66 reinforced with CF, and ground CF were mechanically recycled five times. Mechanical and thermal properties were determined after the first injection, as well as after the 1st, 3rd and 5th cycle of mechanical recycling. The values of mechanical properties (modulus, strength, ...) generally deteriorate, while the thermal properties remain almost unchanged. Part of the change is due to polymer degradation and part is due to fiber shortening.

Keywords: mechanical recycling, carbon fiber, PA66, carbon fiber composites, injection molding.

1. INTRODUCTION

Superior properties and an increasing range of applications are the main driving forces of growth in the consumption of carbon fiber reinforced polymer composites (CFRP). The combination, as well as individual properties, which include but are not limited to high strength-to-weight ratio, stiffness, good chemical and impact resistance, design flexibility and good processsability, attract a wide range of industries from aerospace, automotive, energy, sports, medical to electronics and others [1–4]. Many are driven by demands of lowering the CO_2 emissions that are easiest to achieve by replacement of traditional materials, most often metals, with CFRPs [3–5]. The global annual demand of 51 kt in 2010 increased to 128.5 kt in 2018 and is estimated to achieve nearly 200 kt in 2023 [6]. Such extensive and still increasing consumption of virgin materials rises environmental concerns due to multiplying both, the manufacturing scrap and the end-of-life of CRFP products waste [3,7]. Moreover, concerns are already backed by the regulation existing in the automotive sector, leading the way for other industries, in European Union requiring at least 85% of vehicles to be reused or recycled since 2015 [7–9].

Considering the existing approaches to recycling the CFRP mechanical recycling has proven to be the most convenient approach due to its economic efficiency, environmental friendliness in sense of energy consumption as well as the absence of need for use of chemicals, and easy implementation of the process in the production [1,2,5,7,8,10–12]. Mechanical recycling is especially well suited for short fiber reinforced thermoplastics since the material can be remelted due to the thermoplastic nature of the matrix and loss of mechanical properties due to the process-related fiber breakage is less extensive compared to long or continuous fiber-reinforced materials [4,5,8,13,14].

Considering the above, the present work is a study of the influence of multiple cycles of mechanical recycling on mechanical and thermal properties of polymer composites and a neat polymer (PA66) as reference. Both polymer composites that were mechanically recycled were reinforced with 30% of carbon fiber that differed in length, PA66CF30 is reinforced with standard short carbon fiber while PA66mCF30 is reinforced with the same proportion of ground carbon fibers, which are shorter in length, simulating the use of recovered carbon fiber.

2. EXPERIMENTAL

2.1. Materials

Commercially available composites in granulate form were provided by Lehmann & Voss & Co., Germany. Granulates were injection-molded using Krauss Maffei CX 50-180 Blue Power injection molding machine with a screw diameter of 30 mm and clamping force of 500 kN. Specimens were injection molded in geometries according to ISO 527-2 (type 1BA), ISO 178, and ISO 179 (unnotched and type A notched specimens) standards.

All materials were injection molded according to the recommended processing parameters for reinforced PA66 provided by the manufacturer. Before injection molding, all the materials were dried in a laboratory oven (Memmert 100-800) at 80 °C below the moisture content of 0.1 wt.%. The processing parameters are presented below:

– temperature profile (from a nozzle to the hopper): 285 °C, 290 °C, 285 °C, 280 °C, and 270 °C,

– feeding stroke: 20 mm,

– decompression: 3 mm,

– screw speed: 80 min^{-1},

– backpressure: 55 bars,

– switch over point: approximately 98 % volume of the filled product,

– injection speed: 50 mm/s, last 2 mm 10 mm/s,

– packing pressure: 80 % of injection pressure for 10 s,

– tool temperature: 90 °C, and

– cooling time: 20 s.

Injection-molded products and sprues of specimens that were selected for testing were ground using Wanner C13.20sv mill and injection molded again, i.e., mechanically recycled. Mechanical recycling was performed five times, while characterization was performed after the 1st, 3rd, and 5th recycling cycle. A list of characterized specimens with corresponding compositions is presented in table 1. Neat PA66 degraded in the early stages and was not feasible to plasticize the granulate using uniform processing parameters, so the screw speed needed to be raised to 100 rpm in the first mechanical recycling cycle and 130 rpm after the second recycling. Further recycling was not feasible, due to the too low viscosity of the melt.

Table 1. *List of samples with corresponding materials and compositions*

Specimen	Material	Composition
PA66	PA66 VZ 150	Neat PA66
PA66-1	PA66 VZ 150 after first cycle of mechanical recycling	Neat PA66
PA66-3	PA66 VZ 150 after third cycle of mechanical recycling	Neat PA66
PA66CF30-1	Luvocom 1/CF/30 after first cycle of mechanical recycling	PA66, 30% CF
PA66CF30-3	Luvocom 1/CF/30 after third cycle of mechanical recycling	PA66, 30% CF
PA66CF30-5	Luvocom 1/CF/30 after fifth cycle of mechanical recycling	PA66, 30% CF
PA66mCF30-1	Luvocom 1-50235 after first cycle of mechanical recycling	PA66, 30% mCF
PA66mCF30-3	Luvocom 1-50235 after third cycle of mechanical recycling	PA66, 30% mCF
PA66mCF30-5	Luvocom 1-50235 after the fifth cycle of mechanical recycling	PA66, 30 % mCF

2.1. Characterization

Injection-molded specimens were conditioned according to ISO 291 (at least 88 h at 50 % ± 10 % RH and 23 °C ± 2 °C) before testing. Mechanical properties, namely tensile modulus, tensile strength, elongation at tensile strength, flexural modulus, and flexural strength were determined using a universal Shimadzu AG-H testing machine plus 10 kN equipped with Shimadzu TRViewX optical extensometer and evaluated using TrapeziumX software, version 1.3.1. Tensile tests were performed according to ISO 527-1 using injection-molded test specimen of type 1BA. Tests were conducted at a crosshead speed of 1 mm/min to the 0.25% strain followed by 50 mm/min until the break. Flexural tests were performed according to ISO 178. Molded specimens of standardized sizes (80 mm x 10 mm x 4 mm) were used and the distance between supports was 64 mm. Flexural tests were conducted at a crosshead speed of 2 mm/min. The impact properties of the specimen were determined using the Charpy method. Measurements were performed according to ISO 179 on a pendulum impact tester LIYI LY-XJJD5. The specimen size was 80 mm x 10 mm x 4 mm. The distance between the supports was 60 mm. All the samples were measured flatwise. The notched specimen had an injection-molded type A notch. A pendulum with an impact velocity of 2.9 m/s and with 5 J energy was used for unnotched specimens and 2 J for notched ones, with the only exception of PA66, where 1 J needed to be used for notched specimens. Influence of the mechanical recycling on viscoelastic properties was studied using dynamic mechanical analysis (DMA). Measurements were performed on Perkin Elmer DMA 8000 equipped with a dual cantilever clamping system with an amplitude of 0.005 mm, frequency of 1 Hz, and heating rate of 2 °C/min in the temperature range from 27 °C to 200 °C.

Thermal properties were determined by dynamic scanning calorimetry (DSC), thermogravimetric analysis (TGA), and thermal conductivity by the Hot Disk method. DSC analyses were performed on Mettler Toledo DSC 2 calorimeter according to ISO 11357 standard. Specimens were heated and cooled two times from 0 °C to 300 °C in a nitrogen atmosphere with a gas flow of 20 mL/min and a heating rate of 10 °C. At the beginning of the measurement, there was 3 min long isothermal segment and after each subsequent heating and cooling, there was 5 min long isothermal step. The specimens weighed between 5 mg and 15 mg and were measured in 40 µl aluminum crucibles. TGA was performed employing Mettler Toledo TGA/DSC 3+ thermosgravimetric analyzer which records the corresponding DSC signal to the TGA measurement as well. Specimens, that weighed between 5 mg and 15 mg, were heated from 40 °C to 600 °C in a nitrogen atmosphere and then heated from 600 °C to 900 °C in an oxygen atmosphere. In both segments, the gas flow was 20 mL/min and the heating rate was 10 °C/min. Thermal conductivity was determined using a HotDisk TPS-1500 analyzer according to ISO 22007-2 standard. For measurement, two injection-molded specimens of 80 mm x 10 mm x 4 mm were placed on each side of the Kapton sensor with a 3.189 mm radius. Due to significant differences in the thermal behavior of materials, the measurement parameters needed to be adapted accordingly. The measurement time was 20 s for each sample, except for PA66-3 where it needed to be increased to 40 s and the power was set to 10 mW for PA66, 8 mW for PA66CF30 and 5 mW for PA66mCF30.

3. RESULTS AND DISCUSSION

3.1. Mechanical properties

Tensile and flexural properties of recycled samples are exhibiting dropping trends corresponding to the number of cycles of mechanical recycling. The highest drop of tensile modulus (Figure 1) was measured at neat PA66 after first recycling which is approximately 37% due to degradation of the matrix. The tensile modulus of carbon fiber reinforced composite (PA66CF30) is surprisingly least affected by mechanical recycling while ground carbon fiber reinforced grade (PA66mCF30) is more affected. Tensile modulus of PA66CF30 after one cycle of mechanical recycling does not even drop and, after five cycles, the drop is only 10.7% while the modulus of PA66mCF30 drops by over 13% after only one cycle and almost 33% after the fifth cycle. Similar patterns can be distinguished for reinforced grades while flexural stiffness of neat PA66 is contrary to tensile strength, which slightly increases. Shear, induced with mechanical recycling, seems to improve the interactions between the carbon fiber and the matrix on the account of the improvement of wettability of the fiber and increase in the surface area at the expense of fiber breakage in PA66CF30. A higher drop of modulus at PA66mCF30 probably occurred due to the more prominent effect of fiber breakage on the effective load carrying capacity of shorter fibers.

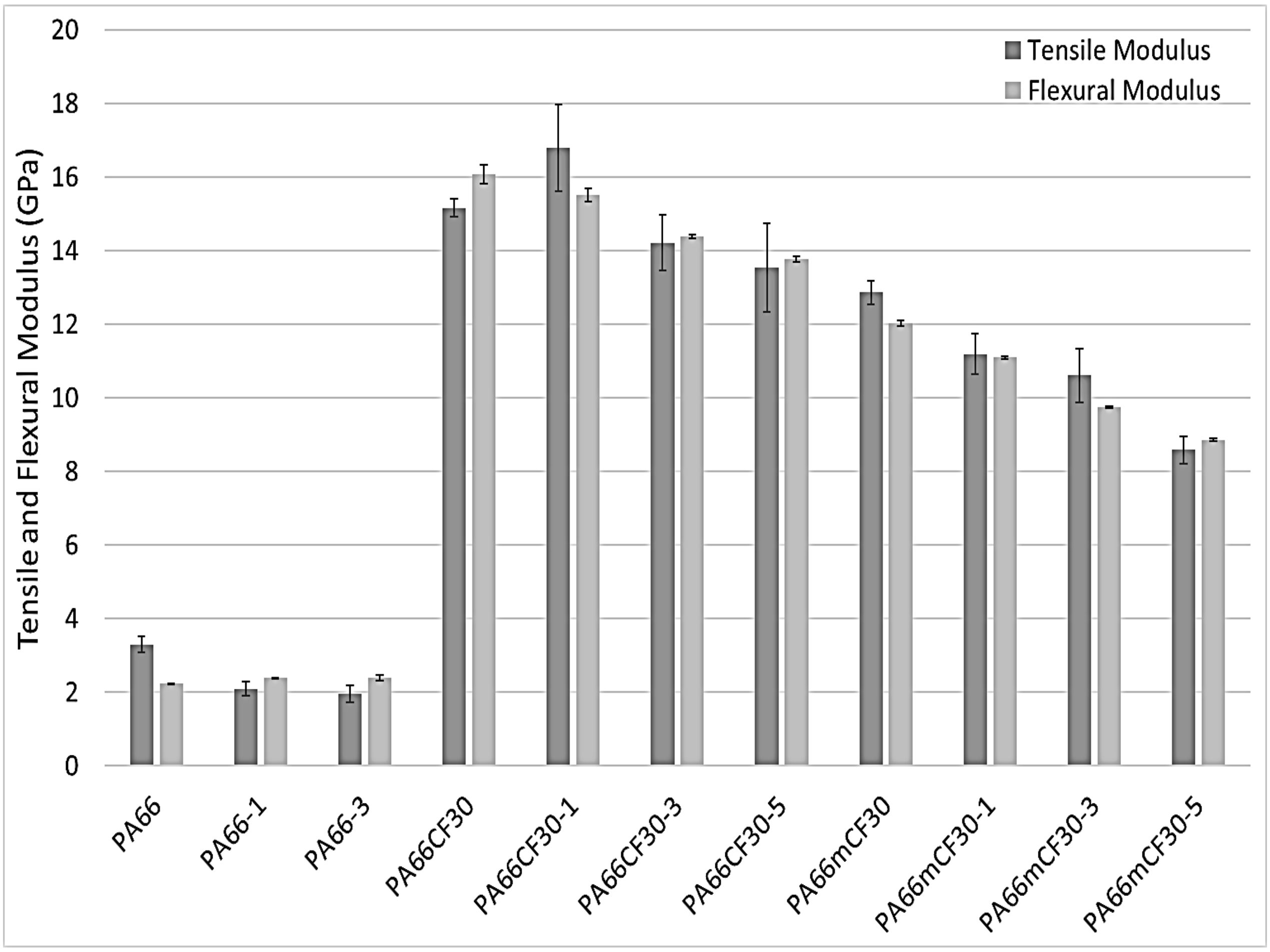

Figure 1. *Comparison of determined tensile and flexural modulus*

Considering the tensile and flexural strength of materials compared in Figure 2, a dropping trend with increased cycles of recycling can be distinguished with reinforced grades while the tensile strength of neat PA66 stays within the same range or even slightly increases due to a decrease in the toughness of the matrix that is corresponding to lower strain at tensile strength (Figure 3) caused by damage induced by grinding and followed repeated injection molding. Both the tensile and flexural strengths of reinforced grades are only slightly affected by the first cycle of recycling, the corresponding drop is below 5%, and after five cycles of recycling, composites still retain about 80% of the tensile strength of virgin material. Regarding the belonging standard deviation of reinforced materials, no significant differences could be found in the determined strains at tensile strengths.

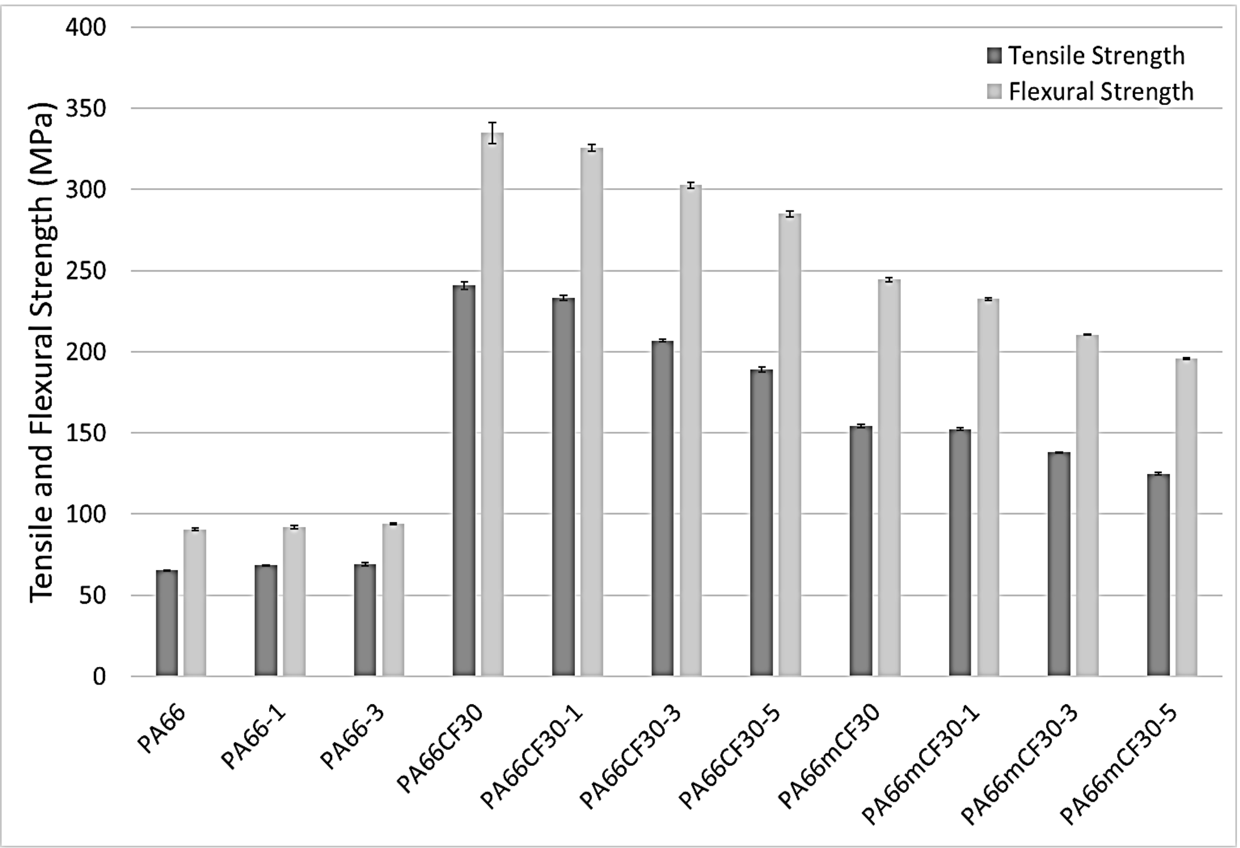

Figure 2. *Comparison of determined tensile and flexural strengths*

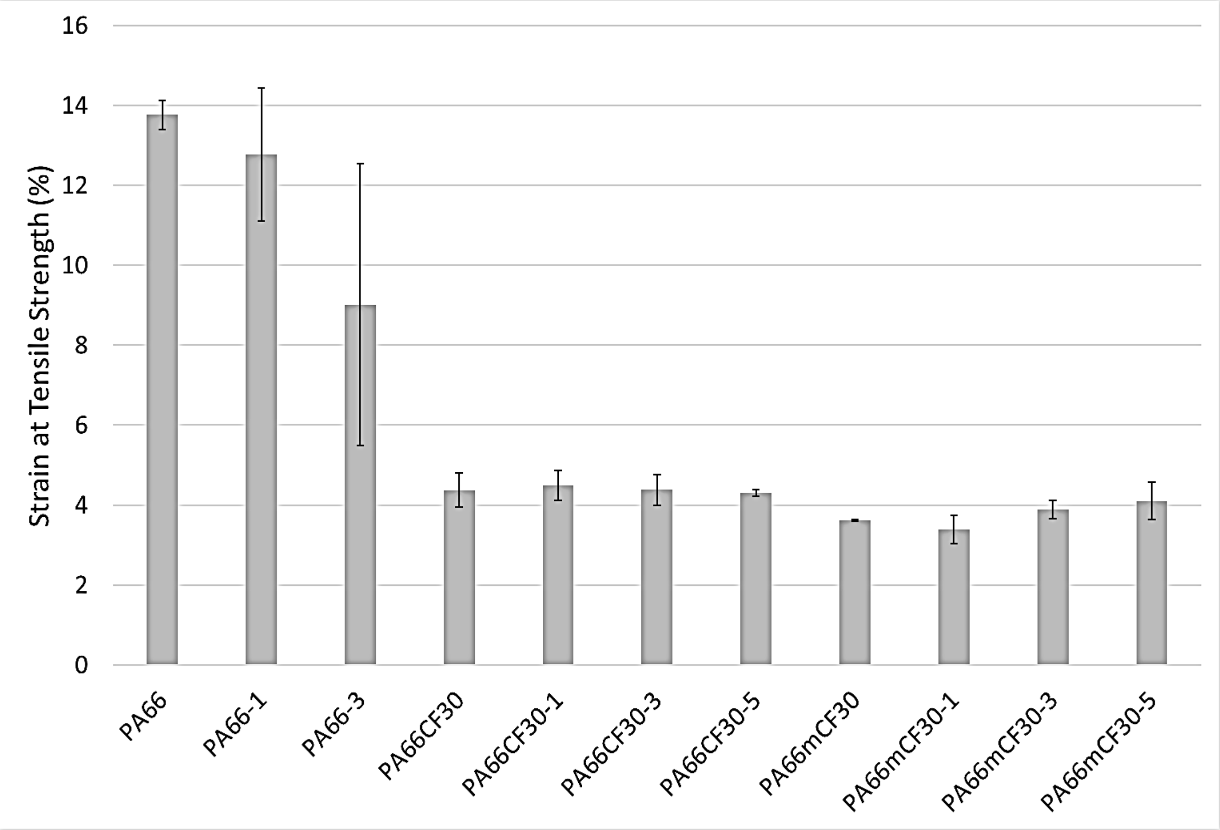

Figure 3. *Strain at a tensile strength*

3.2. Impact properties

Poor impact strength performance of the materials is known to indicate matrix degradation, weak matrix and fiber interactions, and fiber breakage. Virgin PA66 unnotched specimen did not break after the recycling, the specimen fractured during the measurements, meaning that impact strength drastically lowered. Moreover, presumably due to the degradation, specimens fractured unevenly, which resulted in high standard deviations (Figure 4). Moving forward to the reinforced grades, the impact strength of PA66CF30 and PA66mCF30 drops with more recycling cycles, which cannot be claimed due to the differences in the range of standard deviation.

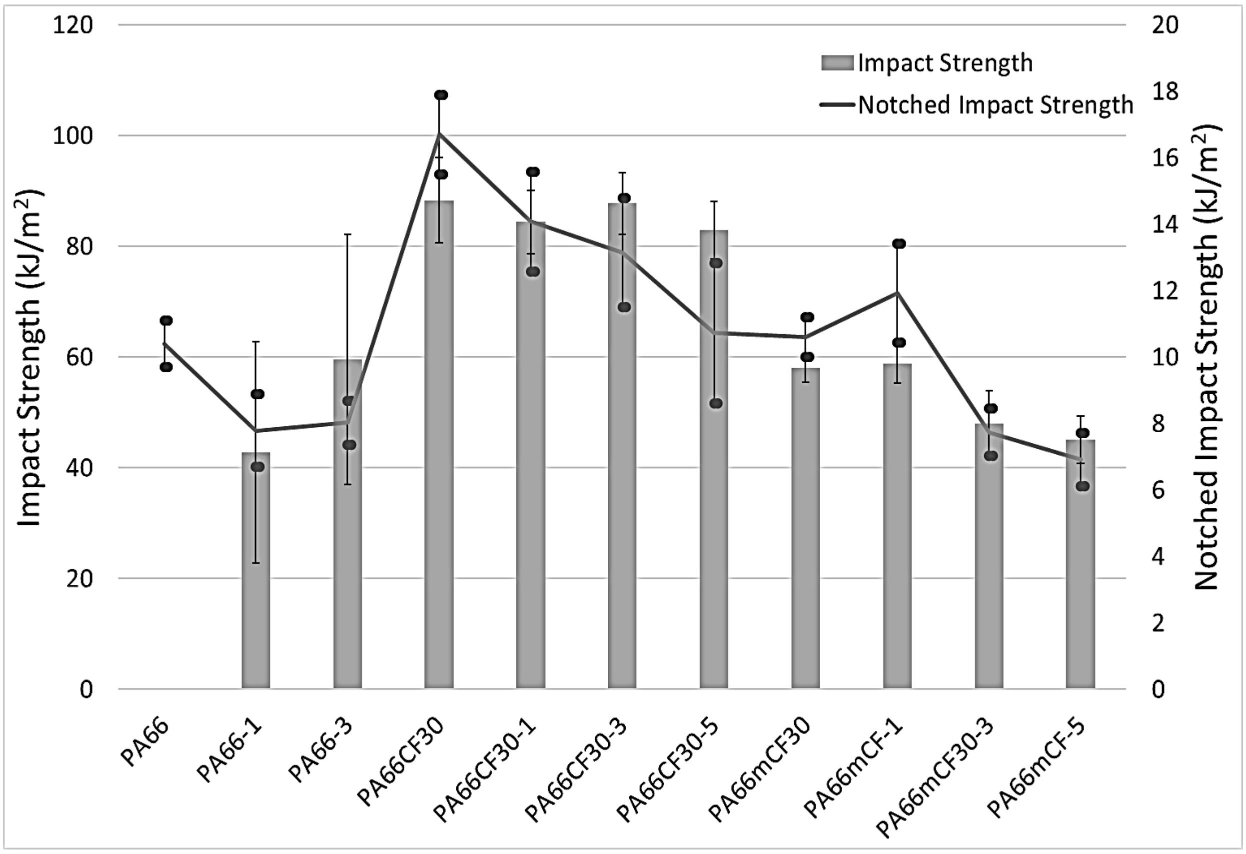

Figure 4. *A graph showing measured Charpy impact strengths and notched impact strengths*

3.3. Thermomechanical properties

Figure 5 shows a storage modulus of specimens measured by DMA at two different temperatures – the first below (30 °C) and the second well above (120 °C) the glass transition temperature of the materials. Influence of the mechanical recycling on the storage modulus is completely consistent with previously noticed patterns at the flexural modulus. The stiffness of recycled PA66 compared to the neat one slightly increases due to polymer degradation. On the other hand, the stiffness of both composites decreases with repeated recycling due to fiber breakage. Compared to virgin material, the decrease is the least significant after the first cycle.

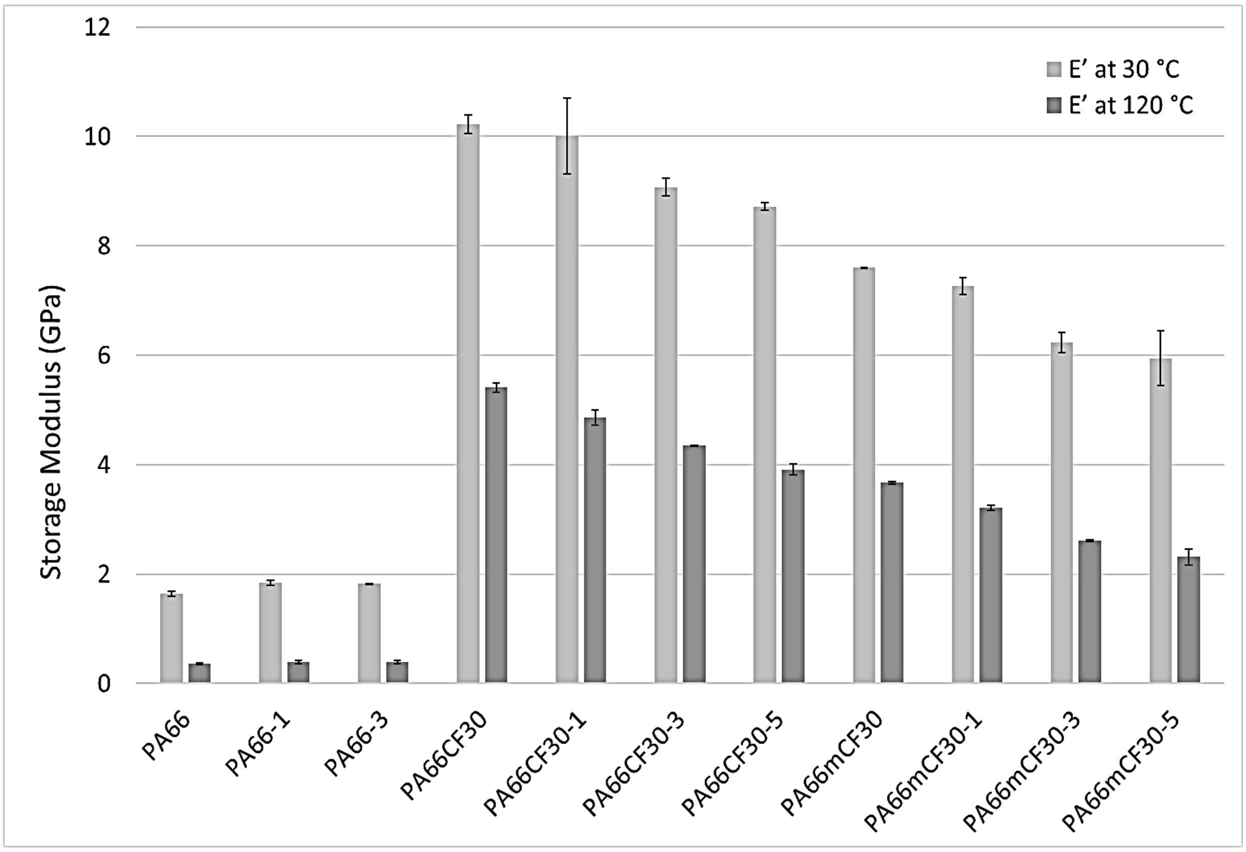

Figure 5. *A graph showing the storage modulus at 30 °C and 120 °C*

3.4. Thermal properties

Evaluation of thermal properties by DSC was focused on the first cooling and second heating scan. The obtained results, including crystallization temperature (T_c), enthalpy of crystallization (ΔH_c), melting point (T_m), melting enthalpy (ΔH_m), and corresponding calculated degrees of crystallinity, are presented in Table 2. Temperatures of the crystallization and melting points were not affected by mechanical recycling significantly since the absolute difference between all 11 measurements was lower than 5 °C considering the crystallization temperature, and 2 °C considering melting points. Similarly, degrees of crystallinity are unaffected by the reinforcement, as well as the mechanical recycling with exception of neat PA66 where a dropping trend is indicated with each recycling cycle. Enthalpies are consistent with the percentage of the PA66 matrix in the sample.

Table 2*. Gathered results of DSC analysis*

Specimen	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)	X_c (%)
PA66	232.2	76.7	262.3	88.9	34.9
PA66-1	233.4	73.7	261.7	74.1	29.0
PA66-3	233.1	69.3	261.6	72.3	28.4
PA66CF30	230.9	44.8	262.0	49.5	27.7
PA66CF30-1	231.0	44.7	261.1	49.5	27.7
PA66CF30-3	231.0	44.2	261.1	49.4	27.7
PA66CF30-5	231.0	40.9	261.1	46.7	26.2
PA66mCF30	234.3	52.0	261.6	52.1	29.2
PA66mCF30-1	233.1	44.0	260.3	51.6	28.9
PA66mCF30-3	233.1	43.2	259.5	52.8	29.6
PA66mCF30-5	232.1	46.4	260.3	52.5	29.4

Employing the TGA, the degradation temperatures presented in Figure 6 were determined. The degradation temperature of neat PA66 evenly decreases with more recycling cycles. Virgin composites have significantly higher degradation temperatures than neat polymers due to the addition of thermal stabilizers that are contained. The temperature drops drastically (by about 20 °C) in the range of neat material after first recycling, which is a perfect example of the working principle of thermal stabilizers that are consumed when the material sustains damage [15].

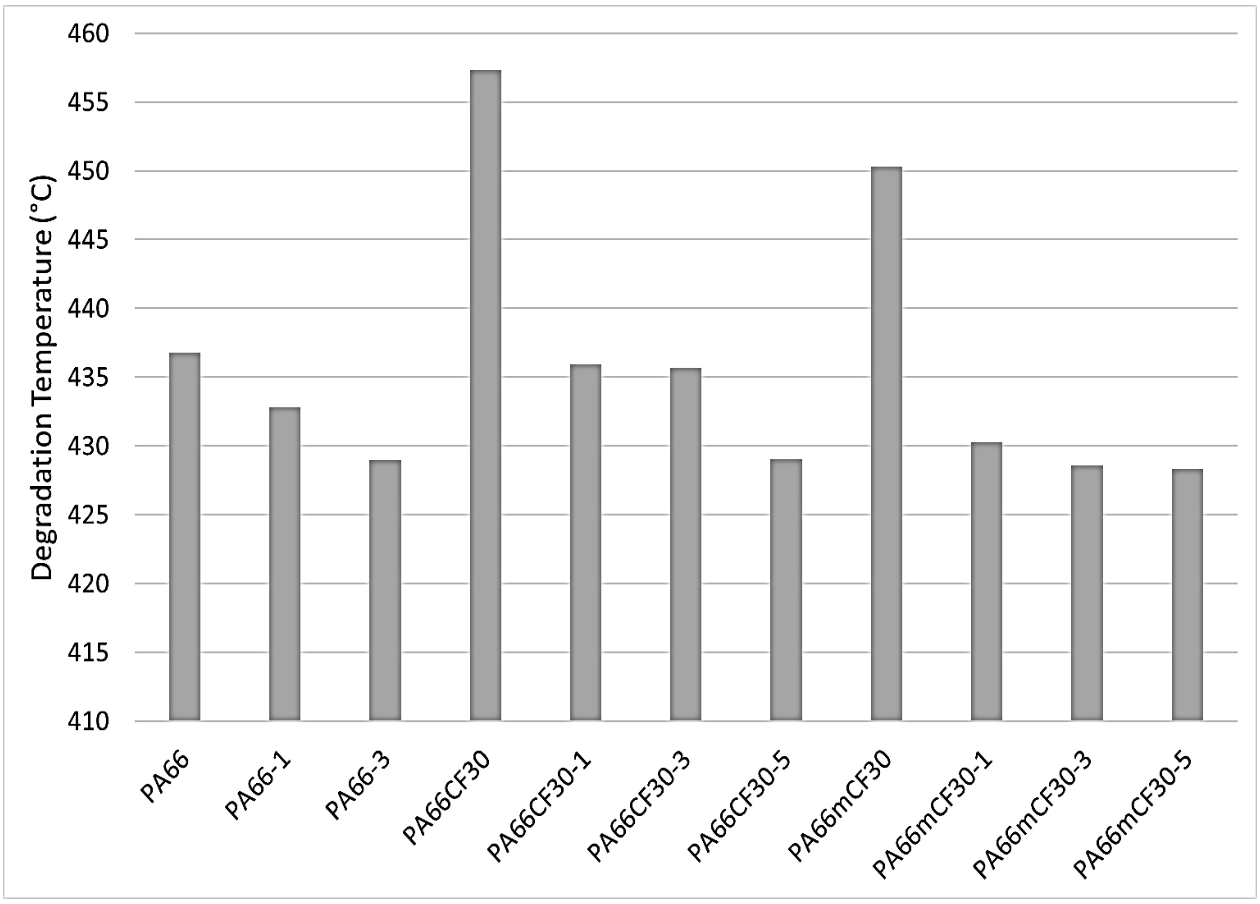

Figure 6. *Degradation temperatures determined by TGA*

Influence of the recycling on thermal conductivity was studied using the HotDisk method and Figure 7 shows the obtained results. The thermal conductivity of PA66 was not significantly influenced. It slightly dropped after the first recycling, corresponding with a lower degree of crystallinity measured by the DSC and increased after the third recycling, presumably due to possible contamination of the material with impurities during the recycling process. The conductivity of PA66CF30 drops with recycling cycles corresponding to the shortening of carbon fiber. However, the thermal conductivity of PA66mCF30 seems to be increased by more recycling cycles, presumably due to orientation and dispersion effects enabled by the lower aspect ratio of the filler, which results in the formation of conductive networks [16].

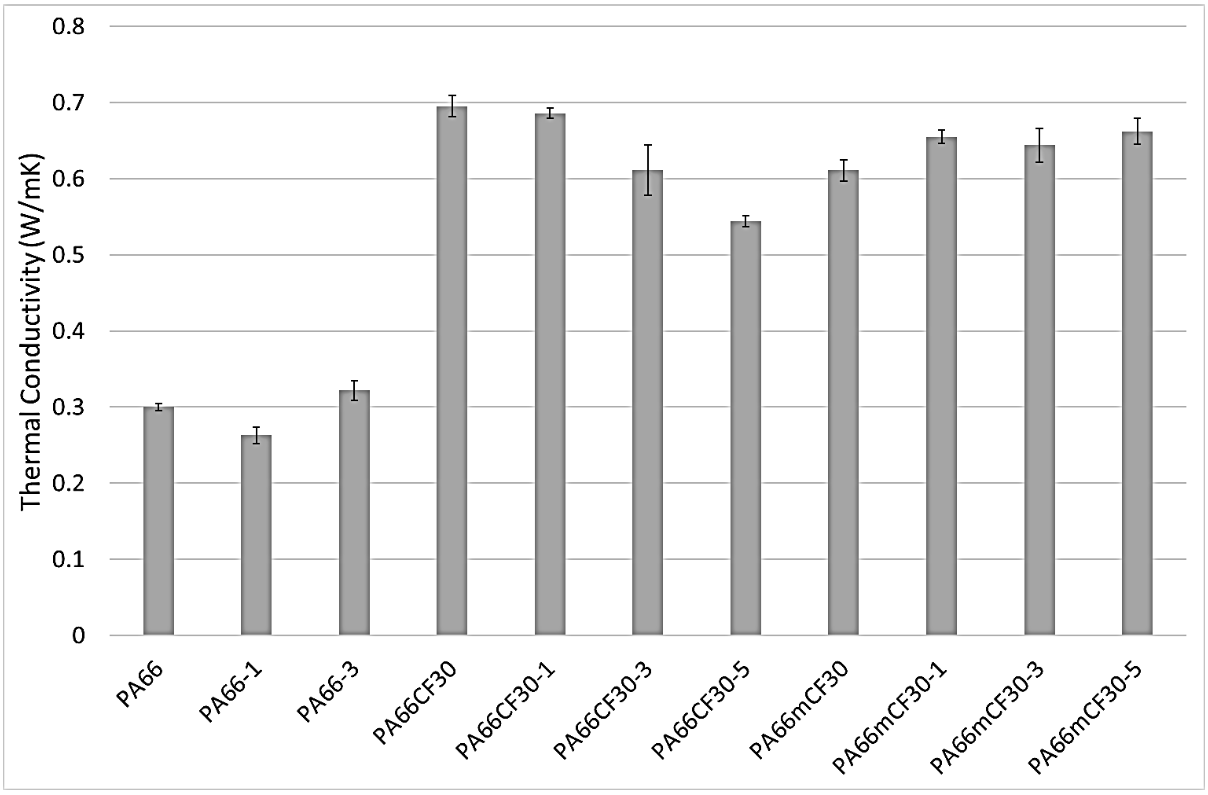

Figure 7. *Thermal conductivities determined by HotDisk*

4. CONCLUSION

This paper evaluates the influence of multiple cycles of mechanical recycling consisting of repeated grinding and injection molding on the mechanical and thermal properties of PA66 and two carbon fiber reinforced PA66 composites differing in the length of fibers. Properties were evaluated for virgin materials, once, three times, and five times for recycled materials. Mechanical properties, i.e., tensile, flexural, and dynamic properties, were influenced by matrix degradation and fiber breakage due to sustained damage caused by the process of mechanical recycling, increasing the stiffness of PA66 and decreasing it in both composites. Similarly, impact properties slightly decreased with more recycling cycles, presumably due to the same reasons. Thermal properties determined by DSC including crystallization and melting were not influenced either by the introduction of reinforcement or mechanical recycling. The degree of crystallization decreases with more cycles for neat PA66; however, composites have a similar degree regardless of the mechanical recycling. Degradation temperatures determined by the TGA minimally decreased with more processing in all the materials. Composites that were additionally thermally stabilized had a significantly higher drop in degradation temperature after first recycling due to the consumption of thermal stabilizers. Thermal conductivity of neat PA66 dropped after first recycling due to a decrease in the degree of crystallinity and increased after the third cycle, presumably due to possible contamination in the process while thermal conductivity of PA66CF30 decreased with more cycles due to fiber shortening. On the other hand, the conductivity of PA66mCF30 slightly increased with more processing due to better and more homogeneous dispersion of the filler.

Overall, mechanical and even less thermal properties of studied materials were influenced by multiple cycles of mechanical recycling. In most cases, the decrease of properties after first recycling was less than 10% and, even after five cycles, they still retained superior properties which leads us to conclude that carbon fiber reinforced PA66 composites are wasted if not mechanically recycled at least once and, preferably, multiple times.

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МЕХАНИЧКО РЕЦИКЛИРАЊЕ PA66, ОЈАЧАНОГ УГЉИЧНИМ ВЛАКНИМА И МЉЕВЕНИМ УГЉИЧНИМ ВЛАКНИМА

Сажетак: Полимерни композити ојачани влакнима заузимају приличан удио у структурним и лаганим примјенама, замјењујући традиционалне материјале кад год је то могуће. Упоредо са многим предностима које нуде, као што су изврсна механичка својства и однос тежине, јефтина и брза производња, могућност прилагођавања својстава за специфичну примјену итд., они обично имају релативно кратак вијек трајања и на крају употребе обично се одлажу на отпад.

Полимерни композити са карбонским влакнима (CFRP) су скупи материјали па треба размислити о њиховој рециклажи и поновној употреби. Зато је проучаван утицај вишеструких циклуса механичког рециклирања кроз мљевење и поновно бризгање. PA66, PA66 ојачани CF и мљевеним CF механички су рециклирани пет пута. Механичка и термичка својства одређена су након првог бризгања, као и након 1, 3. и 5. циклуса механичког рециклирања. Вриједности механичких својстава (модул, чврстоћа, ...) опћенито се погоршавају, док топлинска својства остају готово непромијењена. Дио промјена посљедица је разградње полимера а дио скраћивања влакана.

Кључне ријечи: механичка рециклажа, угљична влакна, PA66, композити од угљичних влакана, инјекцијско прешање.

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